



## DECLARATION

I, Anna Jang, a Korean citizen of 103, Hansvill, 836, Yeoksam-dong, Gangnam-gu, Seoul, Korea do hereby solemnly and sincerely declare as follows:

1. That I am well acquainted with the English and Korean languages.
2. That the following is a correct translation into English of the accompanying certified copy of a Korean Patent Application No. 2002-40105, and I make the solemn declaration conscientiously believing the same to be true.

Seoul, April 19, 2005

A handwritten signature in black ink, appearing to be "Anna Jang", is written over a solid horizontal line.

Anna Jang



## **KOREAN INTELLECTUAL PROPERTY OFFICE**

5           This is to certify that the following application annexed hereto is a true copy  
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Application Number: Patent Application No. 10-2002-0040105

10           Date of Application: July 10, 2002

Applicant(s): Samsung Electronics Co., Ltd.

15                           Dated on August 21, 2002

**COMMISSIONER**

[DOCUMENT] Application for Patent  
[CLASSIFICATION OF RIGHTS] Patent  
[RECEIVING PERSON] The commissioner  
[DATE OF FILING] July 10, 2002  
5 [TITLE OF THE INVENTION-KOREAN]  
단층형 전자사진용 감광체  
[TITLE OF THE INVENTION-ENGLISH]  
Electrophotographic photoreceptor with single layer  
[APPLICANT]  
10 [NAME] Samsung Electronics Co., Ltd.  
[APPLICANT CODE] 1-1998-104271-3  
[APPLICANT]  
[NAME] Cheil Industries Inc.  
[APPLICANT CODE] 1-1998-003453-2  
15 [AGENT]  
[NAME] Hong-sik JEONG  
[ATTORNEY CODE] 9-1998-000543-3  
[GENERAL POWER OF ATTORNEY NO] 2000-046970-1  
[INVENTOR]  
20 [NAME-KOREAN] 임안기  
[NAME-ENGLISH] LIM, AN KEE  
[RESIDENT REGISTRATION NUMBER] 660815-1774524  
[ZIP CODE] 437-010  
[ADDRESS] 332-2, Gochun-dong, Uiwang-city, Gyunggi-do, Korea  
25 [NATIONALITY] KR

[INVENTOR]

[NAME-KOREAN] 이 환구

[NAME-ENGLISH] LEE, HWAN KOO

[RESIDENT REGISTRATION NUMBER] 670923-1056925

5 [ZIP CODE] 440-040

[ADDRESS] 147-2, Sinpung-dong, Jangan-gu, Suwon-city, Gyunggi-do,  
Korea

[NATIONALITY] KR

[EXAMINATION REQUEST] YES

10 [PURPOSE] I, hereby, submit the present application for the Patent and request the  
examination of the present invention under the Article 42 of the Patent Law and the  
Article 60 of the Patent Law.

Attorney

Hong-sik JEONG (seal)

[Official Fee]

15	[Basic fee]	17 pages	₩ 29,000
	[Additional fee]	0 pages	₩ 0
	[Claiming Priority Right]	0 case	₩ 0
	[Filing Request For Examination]	8 claims	₩ 365,000
	[Total]		₩ 394,000

20

## **[ABSTRACT OF THE DISCLOSURE]**

### **[Abstract]**

Provided is a single-layered electrophotographic photoreceptor which has a single-layered structure that includes a charge generating material, a charge transfer material, and a binder resin on a substrate. According to the present invention, the charge generating material is Y form titanyloxy phthalocyanine and the binder resin is polyethylene terephthalate polymer. The single-layered electrophotographic photoreceptor has excellent stability, electrical characteristics, sensitivity and durability.

### **[Search term]**

Electrophotographic photoreceptor, polyethylene terephthalate, Y form titanyloxy phthalocyanine

## **[SPECIFICATION]**

### **[The title of the invention]**

Electrophotographic photoreceptor with single layer

### **5 [Detailed description of the invention]**

#### **[Object of the invention]**

#### **[The field of the invention and the prior art]**

The present invention relates to a single-layered electrophotographic photoreceptor, and more particularly, to a single-layered electrophotographic photoreceptor which is made of a titanyloxy phthalocyanine crystal form as a charge  
10 generating material and a polyethylene terephthalate polymer as a main binder resin.

An electrophotographic photoreceptor is generally made of an inorganic photoreceptor as a charge generator. However, the inorganic photoreceptor has some drawbacks that it is expensive and causes environmental pollution. In order to  
15 overcome these drawbacks, many trials and studies have been conducted mainly with respect to the electrophotographic photoreceptor made of an organic light-electric conductive material. A photoreceptor layer of an organic electrophotographic photoreceptor is formed as an organic light-electric conductive material is dispersed on a resin. Many suggestions have been made with respect to the structure of the organic

electrophotographic photoreceptor layer, such as forming a multi-layered structure having a charge generating layer that is formed by dispersing the charge generating material on resin and with a charge transferring layer that is formed by dispersing a charge transferring material on resin, or forming a single-layered structure in which a charge generating material and a charge transferring material are dispersed on resin concurrently.

In these organic light-electric conductive materials, certain materials are known to have a sensitivity to the light of semi-conductor, which are naphthaquinone group, azo group and phthalocyan group compounds. Especially, in view of sensitivity and chemical and physical stability, the phthalocyan group compounds are used as a blue pigment for ink, paints, and etc. and have been studied widely for a charge generating material.

Generally, the phthalocyan compounds have different UV-absorption spectrums or electrical characters depending on the kind of the central metals. Even the phthalocyan compounds with the same central metal also have different UV-absorption spectrums or the electrical characters depending on their form or size, and the phthalocyan compounds have different characteristics as a charge generating material depending on UV-absorption spectrums or electrical characters. There are non-metal phthalocyanine, chloroaluminum phthalocyanine, chlorogermanium phthalocyanine,

titanyloxy phthalocyanine (TiOPc) in the phthalocyan-charge generating materials. Among them, TiOPc has a high light-sensitivity, diverse crystal forms as other phthalocyanine compounds do. For example, according to the crystal forms of TiOPc, there are  $\alpha$  type TiOPc,  $\beta$  type TiOPc, I type TiOPC, and Y type TiOPc.

5        These phthalocyan charge generating materials are produced and then condensed into crystal form in which a first particle is condensed to several tens of micron. The phthalocyan compound of condensed crystal form is dispersed to be micronized. Then, a dispersion coating liquid is produced from the dispersed crystal form, and then the dispersion coating liquid is spread and used as a film on a  
10        conductive substrate, with the phthalocyan material serving as a charge generating material.

      If a charge generating material in the dispersion coating liquid becomes a macro-particle due to a transformation of the crystal form, growth or a condensation of crystal, the electrophotographic characteristic deteriorates, or a local inequality in  
15        electronic characteristics of the film is caused. Also, with respect to the image quality, image defectiveness such as black spots or fogging, degradation of resolution can be caused. Accordingly, the charge generating material needs to maintain the stability against a transferred crystal form, a growth or a condensation of crystal.

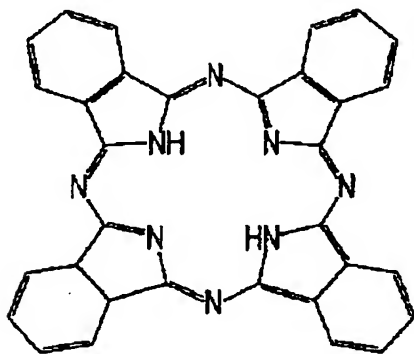
      The binder resin disperses the pigments and allows them to bind evenly to an



aluminum drum. Generally, there are polyvinyl butyral resin, polycarbonate resin, polymethyl acryl resin, polyvinyliden chloride resin that are used for the binder resin. A photoreceptor of an organic light-electric conductive material is the place that is frequently rubbed against papers, electrostatic charge roller, printing roller, and a developing roller. Accordingly, the film of the photoreceptor has some damage and degradation of the electrostatic characteristics if the strength of the photoreceptor is weak. Especially, using the polycarbonate resin for the binder resin, as usually used, will result in weakening of the photoreceptor and subsequent degradation of the electrostatic characteristics of the photoreceptor as the photoreceptor is apt to melt with a paraffin oil, the solvent of a liquid toner of a printing device.

One of the conventional methods uses the dispersion coating liquid including the phthalocyan compound as the charge generating material, which is represented by the following general formula:

[General formula 1]



The dispersion coating liquid is produced by dispersing the X-form H2Pc as the charge generating material together with a polymer such as polyvinyl butyral resin, polyvinyl acetate resin, or the like in a range of concentration of 13wt% to 25wt%.

5 However, this kind of dispersion coating liquid was too difficult to be used for a single-layer electrophotographic photoreceptor and has a rather unsatisfying light sensitivity as a photoreceptor.

The conventional phthalocyan group charge generating material can provide an excellent sensitivity immediately after the production. However, because the crystal  
10 characteristic of the coating liquid state varies by time, the conventional phthalocyan group charge generating material has the shortcomings such as quality unstableness, low productiveness, high costs and etc. Further, demand for the dispersion coating liquid, which is suitable for a single-layered electrophotographic photoreceptor having the binder resin allowing enough resistance of the photoreceptor of the organic  
15 photoreceptor drum, has been constantly increased.

#### **[Technical object of the invention]**

The present invention has been developed in order to solve the above problems in the related art. Accordingly, an aspect of the present invention is to provide an

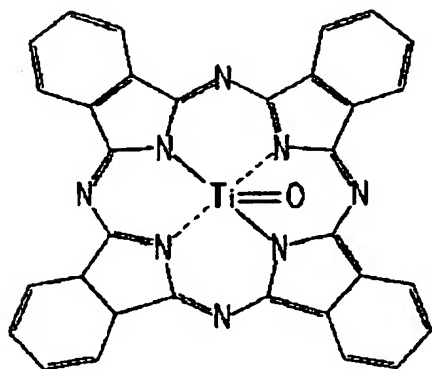
improved single-layered electrophotographic photoreceptor which is made of Y-TiOPc as a charge generating material and polyethylene terephthalate polymer as a main binder resin, to prepare a dispersion coating liquid comprising a charge transfer material. The single-layered electrophotographic photoreceptor has excellent stability and electrical characteristics.

#### [Construction and operation of the invention]

To accomplish the above object, we provide a single-layered electrophotographic photoreceptor comprising a charge generating material, a binder resin and a charge transfer material.

The charge generating material is titanyloxy phthalocyanine of which formula is as follows:

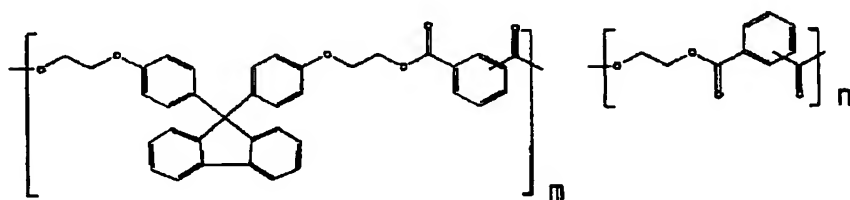
[General formula 2]



The titanyloxy phthalocyanine is a crystal form which has at least 2 main peaks in the range of  $(2\theta \pm 0.2) = 9.5^\circ$  to  $27.3^\circ$  of the Bragg angle in the characteristic  $\text{CuK}\alpha$  X-ray diffraction spectrum.

The binder resin is polyethylene terephthalate polymer of the following  
5 formula:

[formula 3]

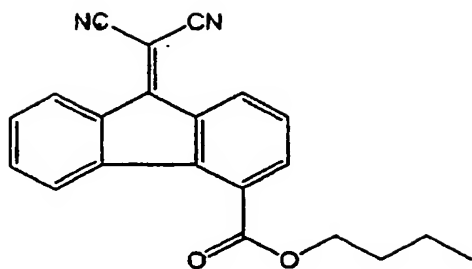


wherein n and m are an integer equal to, or greater than 1.

10 Alternatively, the binder resin can be the mixture of polycarbonate and polyethylene terephthalate polymer mixed with 1:99 to 99:1 in the weight rate.

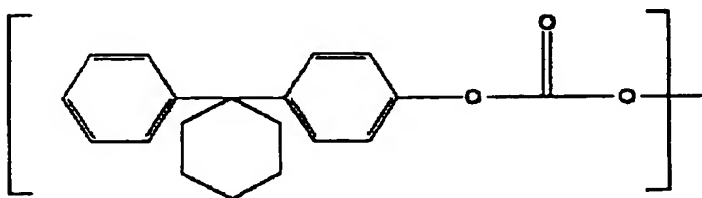
The charge transfer material includes both of positive hole transfer material and electron transfer material. The positive hole transfer material is enaminstylbene polymer, and the electron transfer material is 9-dicyanomethylene-9H-fluorene-4-  
15 carboxylic butyl ester which has the following formula:

[formula 4]



In this invention, the single-layered electrophotographic photoreceptor includes the charge generating material in dispersion liquid. The dispersion liquid  
 5 comprises the charge generating material, 1,1,2-trichloroethane as a solvent, and polycarbonate of the following [formula 5] as a binder resin:

[formula 5]



wherein the polycarbonate is preferably in the range of 10wt% to 90wt%, and  
 10 more preferably, the polycarbonate is in the range of 10wt% to 40wt%.

It is preferable to maintain the temperature below 15°C while milling the dispersion liquid, more preferably, below 5°C.

Reference will now be made in detail to the present preferred embodiments of the present invention.

5        According to the present invention, at first, a dispersion liquid including a charge generating material is made. Then a binder resin and a charge transfer material are added to the dispersion liquid, and the dispersion coating liquid for the single-layered electrophotographic photoreceptor is prepared.

10        The charge generating material used in the present invention is titanyloxy phthalocyanine which has higher sensitivity than non-metal phthalocyan. As for the titanyloxy phthalocyanine crystal form, the present invention uses Y-form titanyloxy phthalocyanine that has at least two main peaks characterized in the range of  $(2\theta \pm 0.2) = 9.5^\circ$  to  $27.3^\circ$  of the Bragg angle in the characteristic  $\text{CuK}\alpha$  X-ray diffraction spectrum. Titanyloxy phthalocyanine is dispersed together with binder resin and  
15        solvent. Here, the binder resin can be polyvinylbutyral resin, polyvinyl alcohol resin, polyamide resin, polyvinyl acetate resin, polyvinyl chloride resin, polyacryl resin, polyurethane resin, polycarbonate resin, polymethylacryl resin, polyvinylidene chloride resin, polystyrene resin and etc., or can be mixture of at least two of the above. Preferably, polycarbonate resin is used.

According to the present invention, the solvent of the dispersion liquid can be 1,1,2-trichloroethane, 1,2-dichloroethane, monochlorobenzene, methylbenzene, ethylbenzene, anisol and etc., or can be mixture thereof. It is preferable to use 1,1,2-trichloroethane.

5 In detail, Y-form titanyloxy phthalocyanine is dispersed for more than 1 hour with a dispersing machine, with addition of binder resin and solvent selected from glass beads, steel beads, zirconia beads, alumina beads, zirconia balls or steel balls. Here, the dispersing machine can be a high-speed agitator, a paint shaker, a ball mill, a sand mill, a dyno mill, a two roll mill, a three roll mill, a supersonic pulverizer, a  
10 ultimizer, and etc. Finally, the dispersion liquid can be obtained by straining out the beads used for the milling through a sieve.

The charge transfer material including positive hole transfer material and electron transfer material, and the binder resin are mixed in the bowl. Then after the mixture is dissolved with the solvent, the dispersion coating liquid can be obtained as  
15 the dispersion liquid is added to the mixture solution. Preferably, the positive hole transfer material is enaminstylbene and the electron transfer material is 9-dicyanomethylene-9H-fluorene-4-carboxylic butyl ester.

The binder resin of the dispersion coating liquid can be a polyethylene terephthalate polymer, differing from the binder resin of the dispersion liquid. Finally,

the single-layered electrophotographic photoreceptor is obtained by coating the dispersion coating liquid on the substrate, for example, on the aluminum drum.

In the following, the single-layered electrophotographic photoreceptor according to the present invention is shown and described in several examples.

5       As these are described by way of an example, this should not be considered as limiting.

#### {EXAMPLES}

#### 10       **EXAMPLE 1**

The producing milling base using a Y-TiOPc is as the following:

In a reaction bowl, Y-TiOPc, 6.3g was agitated and added with the solution in which 1,1,2-trichloroethane(abbreviated TCE), 59.5g was dissolved with polycarbonate resin(PCZ 200 made in Mitshubishi Chemical Inc.), 4.2g. Then the  
15       solution was dispersed together with the glass beads with paint shaker or milling machine for more than 1 hour at 0°C. The dispersion liquid is obtained after straining the glass beads that are used for the milling through a sieve.

The dispersion coating liquid including the dispersion liquid is produced as the following:



The positive hole transfer material is a MPCT 10(Mitshubishi Paper Mill Co.) that is the charge transfer material of enaminstylbene polymer. The electron transfer material is 9-dicyanomethylene-9H-fluorene-4-carboxylic butyl ester(abbreviated BCMF). The binder resin is an O-PET(Trademark of Japan Kanebo Co.) of polyethylene terephthalate polymer.

MPCT 10 of 35wt%, BCMF of 15wt% and O-PET of 60wt% are mixed in 20ml vial. Methylene chloride(abbreviated MC) and TCE are mixed by 6:4, and dissolved in the mixture in the vial. To this solution, the dispersion base is added, and thus the final form of the coating liquid is obtained.

Then the coating liquid obtained as above is coated on the substrate of aluminum drum into a single-layered electrophotographic photoreceptor.

### **Example 2**

The example 2 uses the same method as that of example 1 except for dispersing the solution using 1,2-dichloroethane(DCE) instead of TCE.

### **Example 3**

The example 3 uses the same method as that of example 1 except for dispersing the solution using monochlorobenzene (CB) instead of TCE.

#### **Example 4**

The example 4 uses the same method as that of example 1 except for dispersing the solution using dichlorobenzene (DCB) instead of TCE.

5

#### **Example 5**

The example 5 uses the same method as that of example 1 except for dispersing the solution using anisole instead of TCE.

10

#### **Example 6**

The example 6 uses the same method as that of example 1 except for using 1,4-dioxane instead of MC.

#### **Example 7**

15

The example 7 uses the same method as that of example 2 except for using 1,4-dioxane instead of MC.

#### **Example 8**

The example 8 uses the same method as that of example 3 except for using

1,4-dioxane instead of MC.

#### **Example 9**

The example 9 uses the same method as that of example 4 except for using

5 1,4-dioxane instead of MC.

#### **Example 10**

The example 10 uses the same method as that of example 5 except for using

1,4-dioxane instead of MC.

10

#### **Comparison 1**

The comparison 1 uses the same method as that of example 1 except for dispersing the solution using 1,3-dioxolane instead of MC.

15

#### **Comparison 2**

The comparison 2 uses the same method as that of example 2 except for dispersing the solution using 1,3-dioxolane instead of MC.

### Comparison 3

The comparison 3 uses the same method as that of example 3 except for dispersing the solution using 1,3-dioxolane instead of MC.

### 5 Comparison 4

The comparison 4 uses the same method as that of example 4 except for dispersing the solution using 1,3-dioxolane instead of MC.

### Comparison 5

10 The comparison 5 uses the same method as that of example 5 except for dispersing the solution using 1,3-dioxolane instead of MC.

The samples of the examples 1-10 and comparisons 1-5 were used to produce an electrophotographic photoreceptor, and the thickness, the coating completeness, and  
15 the electric characteristics of the electro photographic photoreceptor were measured.

The measurements are shown in the [table 1] below:

[table 1]

	Solvent	Co-solvent	Quality	E1/2	Vo	Vd	Vdis	Vr	T
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			of coating	( $\mu\text{J}/\text{cm}^2$ )					( $\mu\text{m}$ )
Example 1	MC(6)	TCE(4)	Good	0.169	493	462	75	32	11
Example 2		DCE(4)	Good	0.218	472	448	95	44	10
Example 3		CB(4)	Good	0.218	503	469	76	29	9
Example 4		DCB(4)	Good	0.182	518	481	72	30	10
Example 5		Anisole(4)	Bad	0.231	487	453	78	31	8
Example 6	1,4- dioxane (6)	TCE(4)	Worst	0.2	533	489	110	46	12
Example 7		DCE(4)	Worst	0.222	468	439	98	44	9
Example 8		CB(4)	Worst	0.269	508	474	122	54	9
Example 9		DCB(4)	Worst	0.22	524	485	112	50	12
Example 10		Anisole(4)	Worst	0.271	491	461	117	52	8
Comparison 1	1,3- dioxolane (across) (6)	TCE(4)	Bad	4.92	724	633	97	85	27
Comparison 2		DCE(4)	Bad	0.647	673	547	96	84	20
Comparison 3		CB(4)	Good	0.485	656	526	96	83	21

Comparison 4		DCB(4)	Bad	4.89	728	650	97	86	24
Comparison 5		Anisole(4)	Good	0.505	663	535	96	82	20

In the above table 1,  $E 1/2(\mu J/cm^2)$  is the photo-sensitivity given by the needed photon energy when the initial charged voltage decreased by 1/2 during exposure.  $V_o$  is the initial electrification electric potential and the  $V_d$  is the electric potential after 1 sec-dark decay.

$V_{dis}$  is light exposing electric potential,  $V_r$  is residual electric potential after the light scanning.  $T(\mu m)$  is the thickness of the coating.

As shown in the Table 1, using the TCE has the best result in terms of sensitivity (Reverse of  $E 1/2$ ).

#### 10 [Effect of the invention]

According to the present invention as described above, the single-layered electrophotographic photoreceptor comprises a charge generating material, a binder resin, and a charge transfer material on a substrate, wherein the charge generating material is Y form titanyloxy phthalocyanine in the milled dispersion liquid, and the binder resin is polyethylene therephtalate. Thus, the single-layered electrophotographic

photoreceptor has excellent stability, electrical characteristics, sensitivity and durability.

Although a few preferred embodiments of the present invention have been shown and described, it would be appreciated by those skilled in the art that changes can be made in this embodiment without departing from the principles and spirit of the invention, the scope of which is defined in the claims and their equivalents.

**[What is claimed is]**

**[Claim 1]**

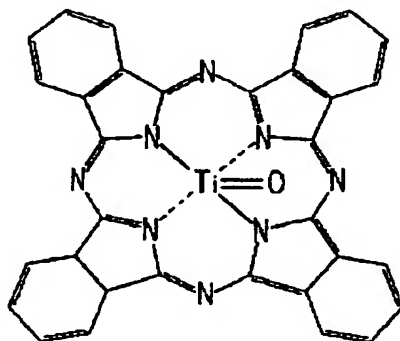
A single-layered electrophotographic photoreceptor comprising:

a charge generating material;

a binder resin; and

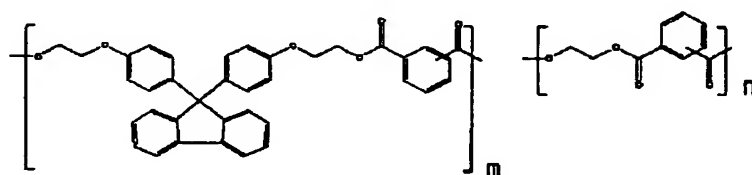
a charge transfer material on a substrate:

wherein the charge generating material is titanyloxy phthalocyanine which has the following formula;



and the titanyloxy phthalocyanine is a crystal form which has at least 2 main peaks in the range of  $(2\theta \pm 0.2) = 9.5^\circ$  to  $27.3^\circ$  of the Bragg angle in the characteristic  $\text{CuK}\alpha$  X-ray diffraction spectrum; and

the binder resin is a polyethylene terephthalate polymer which has the following formula;



with n and m being an integer that is equal to, or greater than 1.

**[Claim 2]**

A single-layered electrophotographic photoreceptor according to claim 1,  
 wherein the charge transfer material comprises the positive hole transfer material and the electron transfer material.

**[Claim 3]**

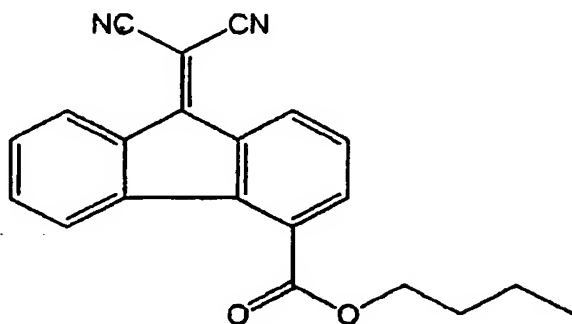
A single-layered electrophotographic photoreceptor according to claim 2,  
 wherein the positive hole transfer material is an enaminstylbene polymer.

**[Claim 4]**

A single-layered electrophotographic photoreceptor according to claim 2,  
 wherein the electron transfer material is 9-dicyanomethylene-9H-fluorene-4-



carboxylic butyl ester which has the following formula:



**[Claim 5]**

A single-layered electrophotographic photoreceptor according to claim 1,

5        wherein the charge generating material is included in a dispersion liquid, the dispersion liquid including the charge transfer material, 1,1,2-trichloroethane as the solvent, and polycarbonate as the binder resin.

**[Claim 6]**

A single-layered electrophotographic photoreceptor according to claim 5,

10        wherein the polycarbonate is in the range of 10wt% to 90wt%.

**[Claim 7]**

A single-layered electrophotographic photoreceptor according to claim 5,

wherein the milling temperature of the dispersion liquid is below 15°C.

**[Claim 8]**

15        A single-layered electrophotographic photoreceptor according to claim 1,

wherein the binder resin is the mixture of polycarbonate and polyethylene

terephthalate polymer in the range of the 1:99 to 99:1 as the weight rate.